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## A Commentary Remark on the Isothermal Crystallization of a Polyethylene Gel from the Stretched Molten State

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The isothermal crystallization of a polyethylene gel from the molten stretched state is briefly discussed in terms of the chain conformation.

### 1. INTRODUCTION

It has been widely observed in many experiments that the kinetic mechanism of the isothermal crystallization of crystalline polymers can be well interpreted by use of the basic concept and equation developed for the crystallization of monomeric substances. However, the crystallization process studied has been concerned with that of crystalline homopolymers mostly from the isotropic molten states, but the crystallization from the anisotropic molten states have not been fully studied as yet. Thus, the kinetic mechanism of the latter process still remains rather obscured. Study of this anisotropic isothermal crystallization is a subject of very significance not only from theoretical point of view but also from the viewpoint of fiber structures, because the structure of all synthetic fibers and natural fibers are generally formed from strained or deformed state.

In the preceding papers, we studied the isothermal crystallization in the extended state of a slightly crosslinked polyethylene as well as the structure and properties of the products from that crystallization<sup>1-4)</sup>. In this short comment, we discuss further several problems appeared in those studies, by using the informations and data obtained afterward.

### 2. ISOTHERMAL CRYSTALLIZATION OF A LIGHTLY CROSSLINKED POLYETHYLENE GEL IN THE UNIAXIALLY ORIENTED STATE

Linear polyethylene, Marlex-50 ( $\bar{M}_v=126,000$ ), was molded to a ring and cross-linked with  $\gamma$ -ray from Co<sup>60</sup> source. The ring samples thus obtained were next extracted with boiling xylene to remove the soluble fraction. The rings of polyethylene gel were stretched to a predetermined length in the molten state and fixed on a glass rod and sealed into the bulb of dilatometer. The samples in the dilatometer were allowed to melt at 170°C for 15 min. before the crystallization, and the volume contraction during the crystallization was observed and converted to

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the crystallinity,  $1-\lambda$ , assuming the additivity of specific volume of the crystalline and noncrystalline phases. The crystallization was conducted in the temperature range of 126–130°C. Typical crystallization isotherms are shown in Figs. 1 and 2.<sup>2,4)</sup> In these Figures some characteristic behavior of the crystallization can be seen in contrast to the crystallization isotherms in the isotropic state. (1) The equilibrium crystallinity is very small, (2) the rate of the crystallization is larger than that of isotropic state at the same temperature, (3) crystallization isotherms are much complicated and show two step equilibriums nearly at 1,000 min and above 20,000 min. But the rate of the crystallization and the equilibrium crystallinity depend on the crystallization temperature in a similar manner as in the

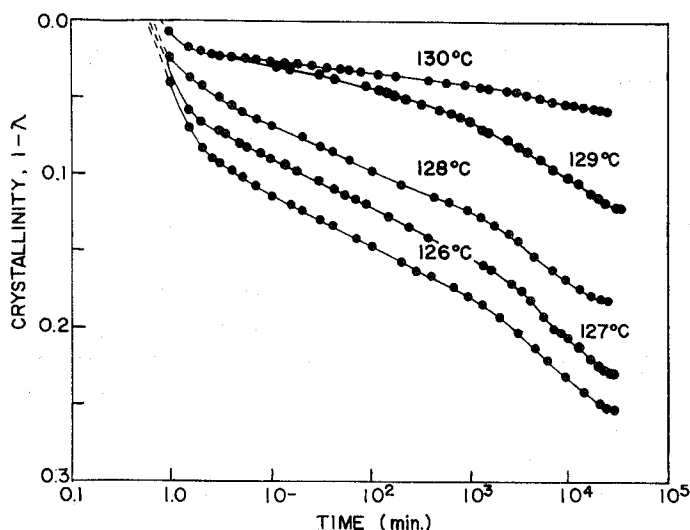


Fig. 1. Crystallization isotherms at indicated temperatures in stretching ratio,  $L/L_0=6.5$ .<sup>2)</sup>

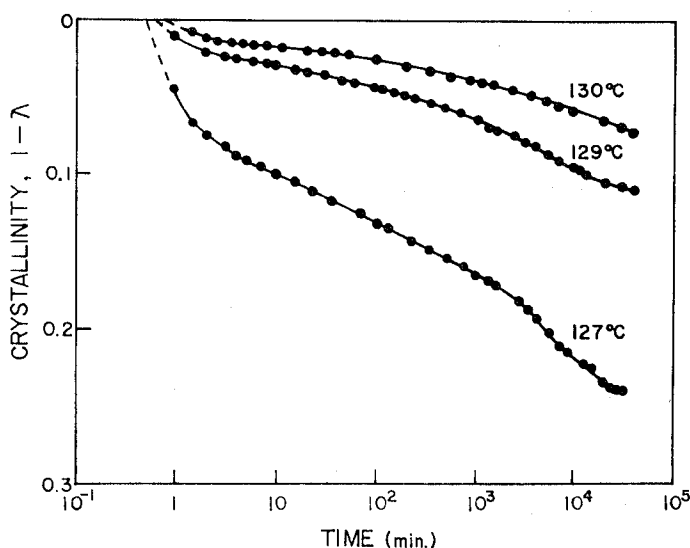


Fig. 2. Crystallization isotherms at indicated temperatures in stretching ratio,  $L/L_0=9.0$ .<sup>2)</sup>

crystallization from the isotropic melt. From the characteristic double S-shaped crystallization isotherms and x-ray diffraction study of the crystalline structure<sup>39</sup>, we have concluded that the crystallization from the stretched state occurs by two steps mechanisms. The first step crystallization is the crystallization procedure in which uniaxially oriented chain segments are involved and the second step is the procedure in which relaxed, essentially isotropic chain segments are involved. The large temperature dependency of the rate of the crystallization and the shape of crystallization isotherm may imply that the isothermal crystallization in the stretched state proceeds with the similar nucleation mechanism as in that in the isotropic melt. The data in Figs. 1 and 2 were re-plotted; the logarithm of the crystallinity,  $\ln(1-\lambda)$ , against the logarithm of time,  $\ln t$ , according to the free growth approximate equation<sup>59</sup> Eq. (1), which has been developed for the isothermal crystallization kinetics of monomeric substances,

$$1-\lambda = kt^n \quad (1)$$

Here,  $k$  is the rate constant,  $t$  and  $n$  are time and the exponential index which is determined by the nucleation mechanism independent of temperature respectively. These plottings showed approximately same inclinations for each isotherm and the value of  $n$  was decided as smaller than 1. But if we examined the data according to the following equation Eq. (2) which was developed by Kitamaru<sup>61</sup>, as describing appropriately the crystallization of polymers, we could obtain the result of  $n=1$ .<sup>4,77</sup>

$$-\ln\left(1-\frac{X}{X(\infty)}\right) + \ln\left[1+\frac{1-X(\infty)}{X(\infty)}X\right] = \frac{2-X(\infty)}{X(\infty)}kt^n \quad (2)$$

The small value of index  $n$  in the crystallization of polyethylene gel in the stretched state is in good accord with the value obtained by Iguchi and Kawai<sup>81</sup> from the study of the stress change accompanying the crystallization in the stretched state of constant length of a crosslinked polyethylene. Furthermore it also agrees with the value obtained by Gent<sup>92</sup> and Mandelkern<sup>103</sup> for the oriented crystallization of rubbery materials. Hence the small value of  $n$  seems to be characteristic generally of the isothermal crystallization in the stretched state of crystalline high polymers. This fact suggests that the mechanism of the nucleation and the growth in the oriented crystallization of polymers is quite different from those of the crystallization in the isotropic state. The value  $n=1$  may indicates that there occurs heterogeneous nucleation with one dimensional linear growth<sup>133</sup> or with diffusion-controlled two dimensional growth<sup>62</sup>.

The over-all rate of the oriented crystallization is larger than that of the isotropic crystallization, if we compare at the same temperature. But in consideration of the results one must take account of the fact that the equilibrium melting temperature in a stretched state is appreciably higher than that in the isotropic state.<sup>11,123</sup> Therefore, in order to estimate the rate of the crystallization, it is necessary to know, first of all, the equilibrium melting temperature in the stretched state. However, since the exact equilibrium melting temperature of polyethylene gel in a stretched state has not been obtained as yet, we should discuss matters here, using the highest melting temperature which was experimentally observed.

In Figure 3, the melting temperatures in stretched states which were measured

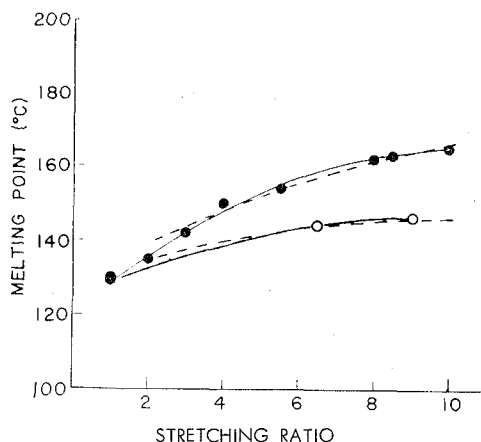


Fig. 3. Relation between melting point and stretching ratio. (●) from birefringence, (○) from dilatometry, and dotted lines indicate theoretical curves after Flory<sup>7)</sup>.

by birefringency and dilatometric technique are shown, but there is seen significant difference between the melting temperatures measured by two methods. If we choose the dilatometric melting temperatures, the rate of the crystallization in a stretched state is nearly equal to that in the isotropic state in a same degree of the supercooling from the melt. This conclusion agrees with the conclusion obtained for *trans*-polychloroprene by Gent<sup>9)</sup>. However, if we adopt the melting temperatures obtained by the birefringence technique, quite contrary conclusion should be reached. Hence final conclusion of this problem must be waited until the exact equilibrium melting temperatures of the system are decided.

### 3. CHAIN CONFORMATION IN THE STRETCHED STATE OF POLYETHYLENE GEL<sup>3)</sup>

The most important factor affecting the oriented crystallization must be the state of the molecular chains in the molten state prior to the beginning of the crystallization. In order to estimate the molecular orientation the total birefringences in molten states of polyethylene gel and the irradiated crude sample were measured for different stretching ratios. Figure 4 shows the total birefringence against the stretching ratio with the theoretical curve calculated by Kuhn and Treloar's equation<sup>14)</sup> which has been derived assuming that all chains\* are stretched in accordance with the macroscopic dimensional change. The experimental curve for the polyethylene gel shows good agreement with the theoretical curve, but the curve for the irradiated crude sample which contains 39% of xylene soluble fraction is appreciably different from the curve for the gel. These results suggest that considerable number of the chains in the irradiated crude sample were not extended by the stretching in the molten state. Assuming that all chains in the soluble fraction and unclosed chains in the gel as well can not be extended by

\* In this paper the term "chian" is defined as part of molecule in the gel or irradiated system, between free end-group ( $-\text{CH}_3$ ) and crosslinked unit, between two free end-groups, or between two crosslinked units whose all intermediate units are composed of methylene units.

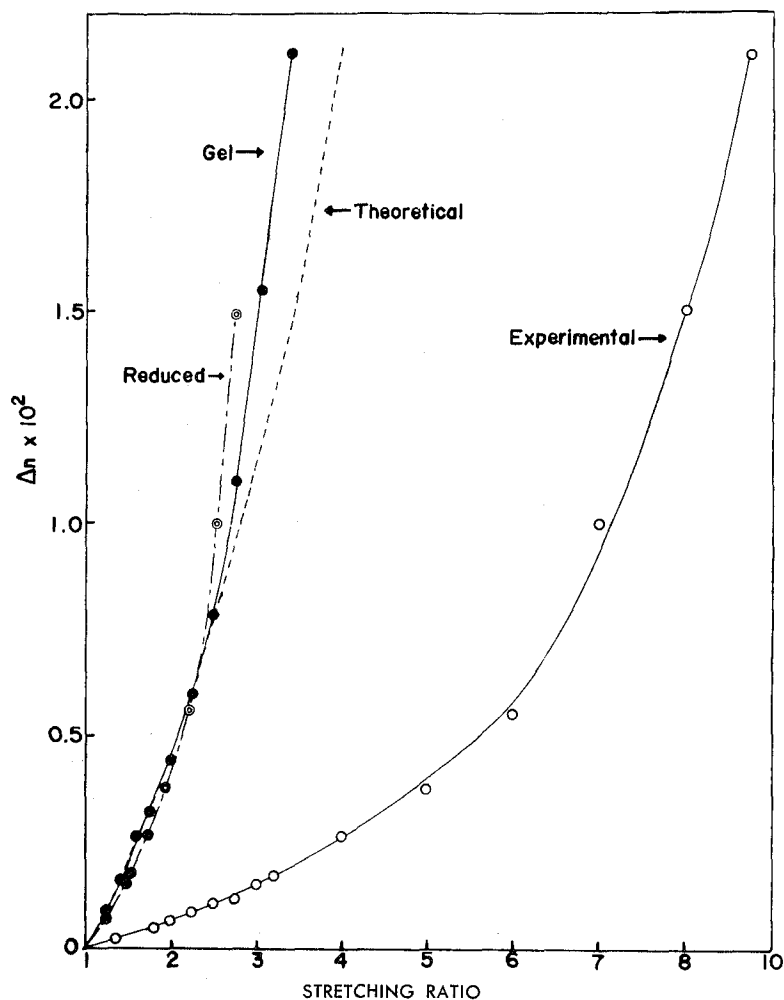


Fig. 4. Change of the total birefringence with stretching at 145°C: (○) irradiated crude sample, (●) gel fraction thereof, (⊙) reduced curve for the irradiated crude sample, (---) theoretical curve for the gel. The crude sample was Marlex-50 irradiated 12.6Mr. by  $\gamma$ -rays and the soluble weight fraction was 0.61<sup>39</sup>.

stretching in the molten state but only closed chains whose both ends are terminated or closed by crosslinking points can be stretched to a stretching ratio corresponding to the macroscopic stretching, we have calculated the effective average stretching ratio for the irradiated crude sample of polyethylene, from the sol fraction and the number of the crosslinking points per one molecule. In Figure 4, the birefringence of the irradiated crude sample in the molten state is plotted also against this reduced stretching ratio. Now, there can be seen the good agreement of the reduced curve with the theoretical curve.

It is concluded from these results that closed chains in the networks of the polyethylene gel could be stretched in accordance with the macroscopic stretching in a molten state as assumed customarily for rubbery materials. Thus we can suppose that the first step of the isothermal crystallization from the melt in the

stretched state must be attributed to the crystallization of the stretched chains of the polyethylene gel.

#### 4. CONFORMATION OF C-C BONDS IN THE POLYETHYLENE GEL IN A STRETCHED STATE

In this section, to simplify matters the following assumptions will be made. (1) The consecutive C-C bonds in *n*-paraffin and polyethylene are only possible in the bond angle of  $109.5^\circ$ , and (2) the rotation of the bonds is only possible in the zigzag *trans* position to the preceding two bonds (*trans*) and in the positions rotated by  $+120^\circ$  or  $-120^\circ$  from the *trans* position (*gauche* or *gauche prime*.) Hereafter, *trans*, *gauche* and *gauche prime* will be abbreviated as *t*, *g* and *g'*. All of C-C bonds in chains of perfectly crystallized polyethylene are in *trans* conformation, but in molten state C-C bonds in molecular chains are composed of a mixed conformation of *t*, *g*, and *g'*. Therefore, it is important to estimate the chain conformation in molten and extended state of polyethylene before the isothermal crystallization under the stretched state to consider the oriented crystallization.

First we discuss the chain conformation of polyethylene in the isotropic state. Consider the chain conformation of *n*-paraffin, the bond number of which is *N* (that is; the carbon number is *N*+1). Then all conformation thereof will be expressed as the permutations whose number of elements is *N*-2 composed of *t*, *g* and *g'*. But, in practice, all of these permutations can not be allowed equivalently. For instance, *gg'* or *g'g* conformations must be disallowed because of the overlapping of hydrogen atoms. The number of the allowed conformations rejecting such disallowed ones was calculated by Smith<sup>15)</sup> for each case of the number of *trans* bonds,  $n_t = 0, 1, 2, \dots, N-2$  for many *n*-paraffins (maximum carbon number=19). If it is assumed that all of the allowed conformations are realized with an equal statistical weight, the average number of *trans* bonds  $n_t$  corresponding to *N* can be calculated. In this case the fraction of *trans* bonds  $f_T$  for linear polyethylene ( $N \cong \infty$ ) was obtained as the extrapolated value of  $\langle n_t \rangle / N-2$  to  $N = \infty^{15)}$ ,

$$f_T = \lim_{N \rightarrow \infty} [\langle n_t \rangle / N-2] = 0.55$$

But it may be supposed that all of the allowed conformation can not happen in practice equivalently, considering the difference of the energy level between *t* and *g* or *g'*. It is well known that the energy level of *g* or *g'* is higher than that of *t*, though the difference of those is not known exactly. If it is assumed that the energy of a chain composed of  $n_t$  *trans* bonds and  $N-2-n_t$  *gauche* or *gauche prime* bonds can be expressed as  $(N-2-n_t) \epsilon$ , where  $\epsilon$  is the energy difference between *t* and *g* or *g'*, then the average value of  $n_t$  will be given as follow,

$$\langle n_t \rangle = \frac{\sum_{n_t=0}^{N-2} n_t M_t(n_t, N) \exp[-\epsilon(N-2-n_t)/kT]}{\sum_{n_t=0}^{N-2} M_t(n_t, N) \exp[-\epsilon(N-2-n_t)/kT]} \quad (3)$$

Here *k* and *T* are Boltzman's constant and absolute temperature respectively, *M<sub>t</sub>* the total number of allowed conformations where the number of *trans* bonds are  $n_t$ . Now, if we use *M<sub>t</sub>* value calculated by Smith, and assume  $\epsilon = 600$  cal/mol =

$9.97 \times 10^{-22}$  cal/bond, the values of  $f_T = \langle n_t \rangle / (N-2)$  can be calculated for every case of  $N \leq 18$  at a determined temperature. Such attempt was made for a voluntary temperature of 420°K.  $f_T$  values thus obtained are found to be approximately in linear relation with  $1/N$  as shown in Figure 5. As the result, the value  $f_T$  for polyethylene was estimated as 0.634 as the extrapolated value to  $N = \infty$ . Thus, it may be supposed that 63.4% of C-C bonds in linear polyethylene are in trans conformation at 147°C. The value of  $f_T$  will increase for larger value of  $\varepsilon$  and smaller value of  $T$ , but in any way, *trans* conformation will dominate C-C bonds over *gauche* or *gauche prime*, at the molten state of polyethylene.

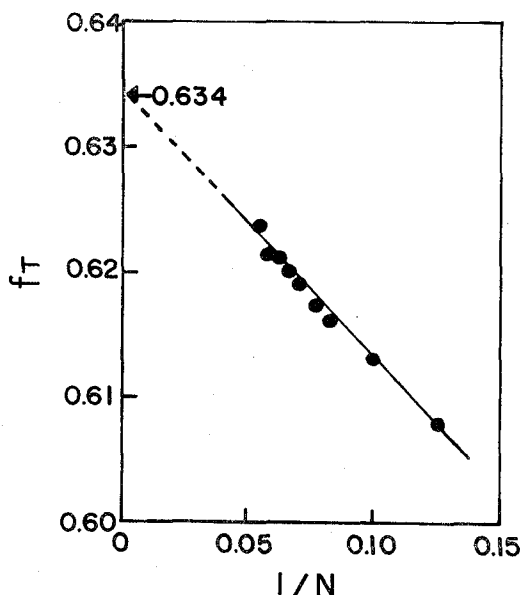


Fig. 5. Bond fraction in *trans* position against  $N^{-1}$ .

Next, we will consider the mean-square end-to-end distance,  $\langle R^2 \rangle$ , of the chains in polyethylene gel in the molten and further stretched states. If the rotation of every bond occurs independently for each other,  $\langle R^2 \rangle$  is given as follow as well known<sup>16,17,18</sup>\*,

$$\frac{\langle R^2 \rangle}{nl^2} = \left( \frac{1 - \cos\theta}{1 + \cos\theta} \right) \left( \frac{1 + \langle \cos\varphi \rangle}{1 - \langle \cos\varphi \rangle} \right) \quad (4)$$

Here  $n$  and  $l$  are number of bonds in the chain and length of the bond respectively,  $\theta$  the bond angle (109.5° for polyethylene), and  $\varphi$  rotation angle of a bond from *trans* position.

If we assume that the rotation of the bond is possible only in the positions of *t*, *g* and *g'*, the average value of  $\cos\varphi$  is given as follow,

\* Another equation between the mean-square end-to-end distance and the chain conformation has been developed by Nagai and other<sup>19</sup> for a little plausibly assumed chains. Some examinations were also made in a similar manner as described below using the relation developed by them. However, the results such as shown in Fig. 6 were not appreciably altered. Hence, in this paper Eq. (4) will be used for further discussions because of the simplicity and easiness of use.



$$\langle \cos \varphi \rangle = f_T \cos \varphi_t + \frac{1}{2}(1-f_T)(\cos \varphi_g + \cos \varphi_{g'}) \quad (5)$$

Here,  $\varphi_t = 0^\circ$ ,  $\varphi_g = 120^\circ$ ,  $\varphi_{g'} = -120^\circ$  for linear polyethylene. Thus, we obtain

$$\langle \cos \varphi \rangle = 1.5f_T - 0.5 \quad (6)$$

Substituting the values, 0.55 and 0.643 for  $f_T$  which have been presumed for the molten state of polyethylene into Eq. (6), we obtain 0.325 and 0.465 as  $\langle \cos \varphi \rangle$  respectively, which give the value of  $\langle R^2 \rangle / nl^2$  as 3.93 and 5.47 respectively from Eq. (4). This implies that the mean square end-to-end distance of the chain in which only *t*, *g* and *g'* configurations are allowed and the bond angle of which is  $109.5^\circ$  is 3.93 or 5.47 times larger than that of the freely jointed chain.

Finally we consider the chain conformation of uniaxially oriented ideal network composed of such chains as mentioned above. From the assumption for ideal rubber elasticity, the mean-square end-to-end distance of the chain increases to  $(\alpha_x^2 + 2\alpha_x^{-1})/3$  times corresponding the macroscopic one dimensional stretching to  $\alpha_x$  times. Then, for the stretched chain, the following relations will be obtained with Eq. (4), (6), respectively, for  $f_T = 0.55$

$$3.93 \times \frac{(\alpha_x^2 + 2\alpha_x^{-1})}{3} = 2.0 \times \frac{(0.5 + 1.5 f_T)}{(1.5 - 1.5 f_T)} \quad (7)$$

and for  $f_T = 0.634$  in the isotropic state,

$$5.47 \times \frac{(\alpha_x^2 + 2\alpha_x^{-1})}{3} = 2.0 \times \frac{(0.5 + 1.5 f_T)}{(1.5 - 1.5 f_T)} \quad (7')$$

These equations represent the relation between  $f_T$  and  $\alpha_x$ , namely the change of weight fraction of *trans* conformation with the uniaxial stretching of polyethylene chain at the noncrystalline state. In Fig. 6,  $f_T$  was plotted against stretching ratio  $\alpha_x$ , according to Eq. (7) and (7').

It is concluded from this result that the conformation of chains stretched

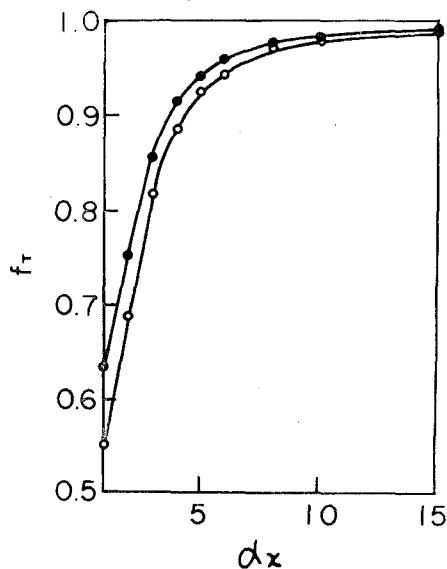


Fig. 6. Bond fraction in *trans* position against stretching ratio. (○) and (●) are calculated according to Eq. (7) and (7') respectively.

uniaxially at the molten state is composed of *trans* conformation of C-C bonds predominantly and particularly in the highly stretched states the *trans* conformation overwhelmingly dominates the system. Furthermore, it suggests that the calculated values of  $f_T$  at the stretched states are not affected so much by the variation of  $f_T$  in the isotropic state (0.55 and 0.643).

#### 4. MECHANISM OF THE ISOTHERMAL CRYSTALLIZATION IN THE STRETCHED STATE

In section 2 and 3, we have shown the typical crystallization isotherms of the polyethylene gel in the stretched states and discussed the chain conformation in the isotropic and stretched states in relation to the oriented crystallization. Although there remain many problems obscured which must be made clear in order to obtain the precise conclusion for the mechanism of the oriented crystallization, here we will present a very brief comment about the mechanism of the oriented crystallization mainly based on the experimental data and theoretical considerations. The isothermal crystallization in the stretched state could be well described by the modified Avram's equation<sup>6)</sup> in spite of the small value of  $n$ , and the rate of crystallization showed a great dependence on the crystallization temperature. These facts imply that the crystallization in the stretched state will be promoted with a nucleation mechanism like the crystallization in the isotropic state, though the detailed feature of the mechanism of the two is very different each other. The crystallization in the highly stretched state, particularly in the incipient stage will be intermolecular crystallization accompanying the decrease of the lateral dimension. This assumption may be strongly supported by the aforementioned theoretical consideration that the major portion of the highly stretched chains is in *trans* conformation at the molten state.

This situation will be at least true for the crystallization in the step of the nucleation. The slow rate of the crystallization and the low degree of the equilibrium crystallinity may be understood as a result of the characteristic oriented crystallization and partly as the result that the system contains crosslinking point. In the oriented crystallization the crystallites born may be jointed each other with many amorphous chains, and in the opposite the amorphous chains may be jointed with the crystallites. These remaining amorphous chains will be relaxed with the proceeding of the crystallization and become unable to crystallize with ease at such high temperatures where only stretched chains can be crystallized.

As the conclusion, considering the predominance of *trans* conformation in the molten and particularly stretched states and the low degree of the equilibrium crystallinity in highly oriented states, the regularly folded intramolecular crystallization such that supposed for the crystallization from dilute solutions by some investigators must be denied at least in the case of the crystallization in the stretched states.

However, the small value of parameter  $n$  for the oriented crystallization suggests a considerable different feature of the mechanism from that of isotropic crystallization, though both of the crystallizations occur with the similar nucleation mechanism. In order to make clear the mechanism of the oriented crystal-

lization, it seems very important to evaluate the change of free energy parameter of the surface of the crystallite at the nucleation step of the crystallization with the molecular orientation.

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